English Equivalent for JP 51102019

PATENT SPECIFICATION

(11) 1 503 670

1 503 670

(21) Application No. 52222/74 (22) Filed 3 Dec. 1974
(23) Complete Specification filed 1 Dec. 1975
(44) Complete Specification published 15 March 1978
(51) INT CL² C08L 95/00; B01F 17/54
(52) Index at acceptance
C3N 1B3 1C3 1D1T 1D1X 1F3 1G3 1Q1 1QX
B1V 2A1 2D 3D2 3DX
(72) Inventor FRANK ERNST PRONK

(19) THE PATENT OFFICE LONDON

(54) SULPHUR-BITUMINOUS COMPOSITIONS

(71) We, SULPHUR DEVELOPMENT INSTITUTE of Canada (SUDIC), an Institute organised and existing under the laws of Canada, of Suite 830, Bow Valley Square, 202-6th Avenue, S.W., Calgary, Alberta, Canada, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The invention relates to a stabilized binding composition for mineral aggregates in the manufacture of paving mixtures, and its preparations; the invention is further concerned with paving compositions and their preparation; more especially the invention is concerned with compositions comprising emulsions of sulphur in bituminous materials for use as a binder for mineral aggregates in the manufacture of paving mixtures.

Compositions comprising sulphur emulsified in asphalt have been proposed as binders in paving compositions in U.S. Patent No. 2,182,837, however, such binders have not been used to any great extent. These prior binders are of low stability and it is necessary to use them without delay in making paving compositions; this necessitates manufacturing the binder at the paving plant site; and this in turn requires the use of two mixers, a high shear mixer such as a colloid mill to form an emulsion of sulphur in asphalt, and a pugmill to mix the mineral aggregates and the emulsion.

In view of the difficulties experienced when using asphalt-sulphur compositions and, until recently, the ready availability of asphalt at low cost, the industry has favoured the use of asphalt alone as a binder for aggregates in paving compositions.

The invention provides an improved binder composition having greater stability than the aforementioned prior binder compositions; in which the now readily available sulphur is employed in an emulsion with bituminous material thus reducing the quantity of the more expensive bituminous material employed in the paving mixture. In addition, the invention provides a simple procedure for manufacturing such emulsions.

The invention further provides a method of manufacturing a paving composition which avoids the necessity of a preliminary mixing operation to form a sulphur-bituminous emulsion.

It has now been found that a small amount of an organosiloxane polymer will stabilize an emulsion of sulphur and a bituminous material.

According to the invention there is provided a stabilized binder composition for mineral aggregates in the manufacture of paving mixtures comprising an emulsion of sulphur and a bituminous material and an emulsion stabilizing amount of an organosiloxane polymer; in which said bituminous material is a continuous phase and said sulphur is a dispersed phase.

According to another aspect of the invention there is provided a method of preparing a stabilized binder composition for mineral aggregates in the manufacture of paving mixtures which comprises mixing together at an elevated temperature bituminous material, molten sulphur and an emulsion stabilizing amount of a liquid organosiloxane polymer to form an emulsion having a continuous phase of bituminous material and a dispersed phase of molten sulphur.

In another aspect of the invention there is provided a method of manufacturing a paving composition comprising mineral aggregates and the

binder formulation of the invention, which comprises simultaneously mixing together, at an elevated temperature, bituminous material, sulphur, a stabilizing amount of an organosiloxane polymer and a major amount of a mineral aggregate.

In yet another aspect of the invention there is provided a paving composition and a paved surface formed from the paving composition.

In an embodiment of the invention a method is provided for the simple plugged flow blending of the bituminous material and sulphur just prior to the pugmill weigh bucket, in cases where it is desirous to simplify the paving plant modifications necessary, to enable the binder compositions of the invention to be used to prepare paving compositions, and also to maintain the paving plant capacity.

In the emulsions of the invention, the liquid sulphur forms a discontinous phase or dispersed phase in the continuous liquid bituminous phase.

Although the inventors do not wish to be limited to any particular theory, it is thought that the stabilizing effect of the organosiloxane polymer on the sulphur-bituminous emulsion arises from the formation of an insoluble monolayer of the polymer at the liquid interface of the sulphur and bituminous material; the monolayer resulting in a significant reduction in the sedimentation rate of liquid sulphur particles during storage.

A further stabilizing of the sulphur-bituminous emulsion may be due to the formation of a mechanical barrier of the polymer at the sulphur bituminous interface preventing coalescence of the liquid sulphur particles.

In addition the emission of the sulphur gases from the binder is reduced when the polymer is present in the mixture.

Suitably the emulsion binder composition contains about 40% by weight of sulphur and about 60% by weight of bituminous material. Preferably the sulphur content should not be less than 20% and not exceed 50% by weight of the binder and more preferably should be from 30 to 40% of the binder. Generally the ratio of sulphur to bituminous material in the emulsion will not exceed 1:1 and is preferably within the range 43:100 to 67:100.

The paving mixture suitably contains from 85% to 95% by weight of mineral aggregate and 5% to 15% by weight of the binder composition; it will be appreciated that the preferred amounts of the ingredients of the paving mixture composition will be governed by aggregate type and gradation in any particular case.

The organosiloxane polymer is employed in an amount effective to stabilize the emulsion of sulphur in bituminous material. This amount should be effective to prevent any significant sedimentation of liquid sulphur from the emulsion when it is maintained at a temperature of 125°C to 145°C under gentle agitation.

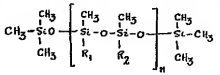
The amount of organosiloxane polymer used does not exceed 0.1%, by weight, based on the weight of bituminous material, and generally amounts of the order of 0.001%, by weight, produce the desired stabilization of the emulsion.

The bituminous materials employed in this invention are bitumen-containing mixtures such as occur in the native state and as a residue from petroleum distillation; a particularly preferred bituminous material is asphalt.

The asphalts employed in the invention should be fluid at the temperatures employed.

Asphalt has a penetration value for paving of from 40 to 400, the penetration grade selected for a specific situation being governed largely by the climatic conditions experienced in the particular area to be paved.

The organosiloxane polymer is a liquid having the general formula



where n ranges from 0 to 1000 and R_1 and R_2 which may be the same or different are selected from the group consisting of alkyl of 1 to 6 carbon atoms, phenyl, benzyl, phenoxy and halo-alkyl of 1 to 6 carbon atoms, for example, CH_3, C_6H_5, or $C_3F_3H_4$. The preferred polymers are fluid polydimethyl siloxanes having the general formula

$$(CH_3)_3\,SiO{-}[SiO.(CH_3)_2]_n{-}Si\,(CH_3)_3$$

where n ranges from 0 to 2000 and particularly suitable are such siloxanes having a viscosity in the range from 50 to 40,000 centistokes, preferably 300 to 12,500 and most preferably of the order of 1000 centistokes at 25°C.

As the mineral aggregate, there may be employed any of the aggregates conventionally used in bituminous paving mixtures, as well as synthetic aggregates Other aggregates considered marginal for conventional paving aggregates may also be used.

The binder compositions of the invention may be prepared by emulsifying the components, the bituminous material being in a fluid or liquid state and the sulphur being in a molten state, in the preferred amounts described above, in a mixer; the organosiloxane polymer and bituminous material are suitably premixed in a suitable fashion. Any type of conventional mixer for producing emulsions may be used, for example a colloid mill. However, the emulsion is readily generated enabling simpler mixing devices to be used. The preferred mixer is a stainless steel "Kenics" Static Mixer which is a simple in-line mixer having no moving parts, mixing being achieved by simultaneous flow division and radial mixing. ("Kenics" is a Trade Mark). The mixing temperature should be in the range where sulphur is in a molten, pumpable state and consequently should be above the melting point of sulphur, 118—119°C; the upper mixing limit is 159°C; above this temperature the sulphur viscosity increases rapidly by several orders of magnitude and it can no longer be pumped. The preferred mixing temperature is in the range 130°C to 150°C.

To store the emulsion, it is transferred to a thermostatically controlled vessel maintained at 125°C to 145°C, where the emulsion is subjected to continuous gentle agitation by for example slowly rotating low pitch propellers of a circulating pump. The emulsion can be stored under these conditions, ready for use as the binder in the formation of a paving composition.

Alternatively, the separate components of the binder composition can be introduced directly and simultaneously into a mixer with the mineral aggregate; and mixed under the conditions indicated above for the emulsion formation; in this case a pugmill is particularly suitable as the mixer.

In order to minimize the modifications of existing paving plants and maintain the plants' normal production capacity, it will generally be desirable to join the molten sulphur stream and that comprising the bituminous material plus organosiloxane polymer just prior to the plant weigh bucket. This can be most effectively achieved, and the emulsion generated at the same time by joining the streams and passing them through a "Kenics" Static Mixer of suitable size upstream from the weigh bucket.

The size of the mixer is governed largely by the required fluid velocity of the sulphur/bituminous material composition through the mixer and is suitably in the range of 1 to 25 ft./sec., preferably of the order of 10 ft./sec.

The binder compositions of the invention are found to have improved storage characteristics as compared with the known sulphur-asphalt binders and exhibit reduced emissions of sulphur gases. Good binder characteristics were demonstrated when the paving compositions were evaluated according to the Marshall Mix Method ASTM D1559. The binder composition further showed good results in freeze-thaw and immersion compression tests performed to evaluate adhesive properties of the binder composition in comparison with conventional paving grade asphalt cement.

Aging studies indicate that sulphur/asphalt emulsion concretes of the invention exhibit increased durability compared to ordinary asphalt concretes. Computer pavement analyses using the CHEVSL program indicate that savings in asphalt concrete layer thickness, and hence savings in materials costs, can be made using the sulphur/asphalt emulsion concretes of the invention.

Marshall stability tests on fresh sulphur-asphalt concretes of the invention show similar values as for comparable asphaltic concretes, however, on curing for a period of two weeks substantial increases are observed in the Marshall Stability of the sulphur asphalt emulsion concretes without an accompanying detrimental decrease in the Marshall Flow. No change in Marshall Stability with time is observed with regular asphaltic concretes.

A particularly important aspect of the binder compositions of the invention is that the sulphur exhibits "super-cooling" i.e. remains liquid below its melting point. Thus paving mixes containing the sulphur asphalt emulsions as the binder retain their workability to lower temperatures than do those containing regular

asphalt binders, with resultant advantages which will be apparent to one skilled in the art.

The invention is illustrated by reference to the following examples which are not to be construed as limiting.

Example 1.

The following ingredients were introduced to a total of 1800 gms into a mixer and emulsified at a temperature of 130°C for 10 minutes.

Liquid sulphur	37.5% by weight
Liquid asphalt ("Gulf" AC500)	62.5% by weight
"Dow Corning" 200 Fluid (trademark for a polydimethyl siloxane)	0.001% (based on the weight of asphalt)

("Gulf" and "Dow Corning" are Trade Marks)

A control was run without the silicone

The mixer was a "Cowles" Dissolver, Model IVG with a "Cowles" Hi-Shear Impeller No. B—1530 (3 in. diameter) operating at a speed of 4400 rpm. ("Cowles" is a Trade Mark). The resulting emulsion was degassed to remove entrained air, and separate samples of the emulsion were stored at 130°C with mild agitation (propeller rotating at 100—125 rpm). Density measurements were made at the top (T) and bottom (B) of three samples to determine whether or not settling was occurring and the results are shown in Table I.

TABLE I

Sample	1/2 hr.		5 hr.		72 hr.	
	T	B	T	B	T	B
Control	1.19		1.05		1.05	
		1.18		1.80		1.80
"Dow Corning" 200	1.19		1.10		1.15	
		1.19		1.21		1.20

The control emulsion had broken within 5 hrs by sedimentation of sulphur as shown by the significant variation in density between the top of each sample and the bottom, whereas the composition of the invention was essentially unchanged after 72 hrs. of heated storage.

Example 2.

A molten sulphur stream and one containing asphalt ("Gulf" AC500 pen 150—200) plus "Dow Corning" 200 Fluid (0.001% by weight of the asphalt) were combined and pumped through a "Kenics" Model 1/2—10—320—0 Static Mixer. This is a one-half inch diameter mixer containing six helical baffles. Fluid stream temperatures were maintained at 138°C. The linear velocity through the mixer was varied from 0.2 to 2.3 ft./sec. and the sulphur content varied between 15% and 85% by weight of the asphalt. Samples of the emulsion prepared in this way were examined for particle size distribution by a photomicrographic technique. In all cases the average particle size was less than 5 microns and the particle size distribution range was narrow.

Example 3.

Paving mixes were prepared by the simultaneous injections of liquid sulphur and asphalt cement containing "Dow Corning" 200 Fluid into a heated aggregate

in a "Hobart" Laboratory Mixer. ("Hobart" is a Registered Trade Mark). The mixing temperature was 138°C and the mixing cycle was 60 seconds. The mix composition was as follows:

Asphalt Cement ("Gulf" AC500 penetration 150—200)	4.5 parts by weight
Liquid Sulphur	3.0 parts by weight
"Dow Corning" 200 Fluid	.001% by weight of the asphalt
Aggregate (well graded 3/8")	92.5 parts by weight

A control mix containing 6.5 parts of asphalt and no sulphur was prepared and also a mix where the sulphur and asphalt had been pre-emulsified in a "Kenics" Static Mixer. The samples were evaluated using the Marshall Method. The asphalt control was compacted at 127°C and 35 blows/face were applied whereas the emulsion samples were compacted at 121°C and 30 blows/face. The results are shown in Table II.

TABLE II

Sample Type	Marshall Stability — lbs.		Flow — 0.01 ins.	
	24 hrs. after moulding	14 days after moulding	24 hrs. after moulding	14 days after moulding
S.A.	2050	3420	9.5	12.5
S.A. pre-emulsified	2690	4250	9.0	11.0
Control	2050	2050	12.0	12.0

S.A. denotes sulphur-asphalt emulsion of the invention.

The initial compaction temperature of 121°C for the sulphur-asphalt samples ensures that the temperature of the sample will fall below the melting point of sulphur during compaction. If solidification of the sulphur occurs during compaction the samples will lose compactability and this will be reflected in lower densities and Marshall stabilities. The data in Table II indicates that freezing has not occurred during compaction. Although the sulphur-asphalt sample which was not pre-emulsified had a somewhat lower Marshall stability compared to the pre-emulsified sample, the 24 hr. value was quite high and the characteristic increase in the Marshall Stability was observed over the 14 day period.

Example 4.

A paving mix was prepared using a 2000 lb. asphalt paving batch plant. The mix composition was as follows:

Asphalt Cement ("Gulf" AC500 1500—200 pen)	4.53 parts by weight
Sulphur	2.67 parts by weight
"Dow Corning" 200 Fluid	0.001% by weight of the asphalt
Aggregate (Well graded 1/2 inch)	92.8 parts by weight

The asphalt stream containing the organosiloxane polymer was combined with the molten sulphur stream and passed through a "Kenics", model KMOD—10 mixer. This is a 1-1/2 inch diameter unit containing six helical elements or baffles. The asphalt and sulphur were maintained at 138°C and the velocity through the mixer was 18 ft./sec. The sulphur-asphalt emulsion was metered into a pugmill containing the heated aggregate (149°C) and the emulsion

and aggregate were mixed for 30 seconds. Mix samples were subjected to evaluation by the Marshall Method ASTM D1559; the results are tabulated in Table III.

TABLE III.

Marshall Stability — lbs.		Flow — 0.01 ins.	
24 hrs. after moulding	14 days after moulding	24 hrs. after moulding	14 days after moulding
2530	2660	8	10
2320	3040	9.5	9.5

Example 5.

A durability study was aimed at establishing the change in stiffness of asphaltic concretes containing normal weight and lightweight aggregate filler with asphalt as the binder and with a stabiliser binder composition of the invention as the binders.

Prior to placing the samples in the test environments, the resilient modulus, M_R, and the density of each sample were determined. Samples were place in a dry environment at each of two temperatures, 0°F and 140°F, for a period of seven months. It has been shown that for ordinary asphaltic concrete, storage for seven months at 140°F is equivalent to 5 to 7 years aging in terms of recovered asphalt viscosity. The second temperature of 0°F was used to determine the M_R changes for the low temperature service extreme for asphaltic concretes. The results are shown in Tables IV and V.

TABLE IV

RESULTS OF STORAGE AT 0°F

Sample Type	Original M_R (x 10^5 psi)	Final M_R (x 10^5 psi)	Final M_R as % of Original
Emulsion A	3.86	2.79	72.3
Asphalt only A	1.29	0.79	61.6
Emulsion B	3.90	3.49	89.4
Asphalt only B	1.13	0.66	58.2

A — denotes a normal weight aggregate
B — denotes a lightweight aggregate
Emulsion — denotes a stabiliser binder composition of the invention.

TABLE V.

RESULTS OF STORAGE AT 140°F

Sample Type	Original M_R (x 10^5 psi)	Final M_R (x 10^5 psi)	Final M_R as % of Original
Emulsion A	3.72	4.19	112.7
Asphalt only A	1.26	4.66	370.7
Emulsion B	3.94	5.67	143.9
Asphalt only B	0.93	3.06	328.5

Consideration of Table IV shows that at 0°F there is a reduction in the M_R of all the specimens.

However, the sulphur-asphalt emulsion concrete specimens of the invention show a greater retention of strength compared to regular asphalt concretes.

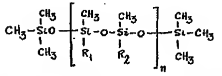
At 140°F, Table V, it is clear that the increase in strength of the sulphur-asphalt emulsion concrete specimens is proportionately much less than that for the ordinary asphaltic concrete specimens.

This indicates less aging (hardening) of the sulphur-asphalt emulsion concretes and suggests better durability properties than their ordinary asphalt counterparts.

WHAT WE CLAIM IS:—

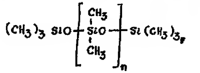
1. A stabilized binder composition for mineral aggregates in the manufacture of paving mixtures, comprising an emulsion of sulphur and a bituminous material and an organosiloxane polymer in an amount of not more than 0.1% by weight, based on the weight of the bituminous material, in which said bituminous material is a continuous phase and said sulphur is a dispersed phase.

2. A composition according to claim 1 in which said polymer has the general formula:



where n ranges from 0 to 1000 and R_1 and R_2 which may be the same or different are selected from the group consisting of alkyl of 1 to 6 carbon atoms, phenyl, phenoxy, benzyl and halo-alkyl of 1 to 6 carbon atoms.

3. A composition according to claim 1 in which said polymer has the formula



where n ranges from 0 to 2000 and has a viscosity of 300 to 12,500 centistokes at 25°C.

4. A composition according to claim 1, 2 or 3 comprising 60 to 70%, by weight, of said bituminous material and 30 to 40% by weight, of said sulphur based on the weight of said composition; and not more than 0.1%, by weight, of said polymer based on the weight of said bituminous material.

5. A composition according to claim 4 wherein said bituminous material is asphalt and said polymer is present in a stabilizing amount of about 0.001%, by weight, based on the weight of asphalt.

6. A paving mix suitable for forming a paved surface comprising from 85% to 95%, by weight of mineral aggregate and from 5% to 15%, by weight of a binder composition; said binder composition comprising an emulsion having a continuous phase of bituminous material and a dispersal phase of sulphur and containing an organosiloxane polymer in an amount of not more than 0.1%, by weight, based on the weight of the bituminous material.

7. A paving mix according to claim 6 in which said binder composition comprises 60 to 70%, by weight, of said sulphur bituminous material and 30 to 40%, by weight,of said sulphur based on the weight of said composition; and not more than 0.1%, by weight, of said polymer, based on the weight of said bituminous material.

8. A paving mix according to claim 6 or 7 wherein said bituminous material is asphalt and said polymer is present in a stabilizing amount of about 0.001%, by weight, based on the weight of asphalt.

9. A paving mix according to claim 6, 7 or 8 in which said polymer has the formula

$$(CH_3)_3\,SiO\left[\begin{array}{c}CH_3\\ |\\ SiO\\ |\\ CH_3\end{array}\right]_n Si\,(CH_3)_3$$

where n ranges from 0 to 2000 and is selected such that the polymer has a viscosity of 300 to 12,500 centistokes at 23°C.

10. A paved surface formed from a paving mix according to any of claims 6 to 9.

11. A method of preparing a stabilized binder composition for mineral aggregates in the manufacture of paving mixtures which comprises mixing together at an elevated temperature bituminous material, and molten sulphur, together with a liquid organosiloxane polymer, in an amount of not more than 0.1%, by weight, based on the weight of the bituminous material, to form an emulsion having a continuous phase of bituminous material and a dispersed phase of molten sulphur.

12. A method according to claim 11 in which the ingredients are mixed to form an emulsion containing 60 to 70%, by weight, of said bituminous material and 30 to 40%, by weight, of said sulphur based on the weight of said composition; and not more than 0.1%, by weight, of said polymer, based on the weight of said bituminous material.

13. A method according to claim 11 or 12 in which said polymer has the formula

$$(CH_3)_3\,SiO\left[\begin{array}{c}CH_3\\ |\\ SiO\\ |\\ CH_3\end{array}\right]_n Si\,(CH_3)_3$$

where n ranges from 0 to 2000 and has a viscosity of 300 to 12,500 centistokes at 25°C.

14. A method according to claim 11, 12 or 13 wherein said mixing is at a temperature of from 130°C to 150°C.

15. A method according to any of claims 11 to 14 including maintaining the resulting emulsion in a thermostatically controlled storage vessel at a temperature of 125°C to 145°C under gentle agitation.

16. A method according to any of claims 11 to 15 wherein the ingredients of the composition are passed through an in-line static mixer having a plurality of baffles adapted to produce flow division and radial mixing of the composition, said bituminous material containing said organo-siloxane polymer, and sulphur being combined at a point immediately prior to said mixer.

17. A method according to claim 16 wherein said ingredients flow through said static mixer with a fluid stream velocity in the range of 1 to 25 ft/sec.

18. A method of preparing a bituminous paving mixture comprising simultaneously mixing at an elevated temperature from 85 to 95%, by weight, of a mineral aggregate and 5 to 15% of a binder composition comprising a liquid bituminous material, liquid sulphur and an organosiloxane polymer in an amount of not more than 0.1% by weight, based on the weight of the bituminous material.

19. A method according to claim 18 wherein said mixing is in a pugmill and said bituminous material containing said polymer and said sulphur are introduced simultaneously into the pugmill containing the mineral aggregate.

20. A method according to claim 19 wherein said bituminous material and said sulphur are introduced into a static mixer having a plurality of baffles adapted to produce flow division and radial mixing, at a point immediately prior to said pugmill.

21. A stabilized binder composition according to claim 1, substantially as hereinbefore described and exemplified.

22. A paving mix according to claim 6, substantially as hereinbefore described and exemplified.

23. A method according to claim 11 for preparing a stabilized binder

composition, substantilly as hereinbefore described and exemplified.

24. A stabilized binder composition, whenever prepared by the method according to any of claims 11 to 20 and 23.

VENNER, SHIPLEY & CO.,
Chartered Patents Agents,
Rugby Chambers,
2 Rugby Street,
London, WC1N 3QU.
Agents for the Applicants.

Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1978.
Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.